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OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

**MEMORANDUM**

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SUBJECT: Revised Estimate of Carbaryl Concentrations in Aquatic Environments
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This is the final report for revised estimated environmental concentrations (EEC's) in surface water for the use of carbaryl on selected crops for assessment of aquatic risks. These EEC's are intended to replace those in the *Environmental Fate and Ecological Risk Assessment for the Reregistration of Carbaryl* (Libelo *et al.*, 2002). Since the issuance of that document, new information that has been received by the Agency in response to a request for comments by the Agency, particularly on foliar degradation rates, that warranted a re-evaluation of the aquatic exposure. We have also taken the opportunity to make some other changes that improve the general quality and reliability of the estimates. The EEC's for carbaryl use on representative crops at the maximum label use rates are listed in Table 1. The use of carbaryl on citrus in Florida generated the highest EEC's in this assessment. This is mostly due to the large amount of rainfall in Florida where much of citrus is grown in the United States. In addition tto the EEC's in Table 1, estimates were also made in for an 'average' use pattern, and a 'maximum reported' use pattern for each of these crops. These use patterns and the results of these simulations are discussed in detail in the body of the document. Also EEC's have been calculated for a number of crops grown on the Pacific coast in order to support endangered species assessments.

**Table 1.** EEC's for the 'maximum' use patterns for carbaryl on selected agricultural crops. Endangered species scenarios are for use in evaluating the risks to endangered aquatic species on the Pacific Coast.

| Crop | Peak | 4 Day Mean | 21 Day Mean | 60 Day Mean | 90 Day Mean |
|---|---|---|---|---|---|
| | ---------------------------- $\mu g\ L^{-1}$ carbaryl ---------------------------- | | | | |
| Apples (PA) | 30.6 | 25.646.7 | 14.833.4 | 6.514.6 | 4.4 |
| Citrus (FL) | 152.6 | 135.7 | 82.0 | 41.0 | 29.6 |
| Sweet Corn | 52.7 | 48.8 | 30.2 | 19.2 | 16.6 |
| Field Corn | 46.9 | 41.9 | 24.9 | 14.4 | 10.3 |
| Sugar beets | 23.3 | 20.6 | 12.8 | 6.2 | 4.2 |
| Rangeland | 12.8 | 11.3 | 6.5 | 2.9 | 1.9 |
| Endangered Species Scenarios | | | | | |
| Apples (OR) | 19.2 | 17.0 | 13.0 | 6.3 | 4.3 |
| Blackberries (OR) | 12.4 | 11.0 | 9.5 | 6.2 | 4.3 |
| Citrus (CA) | 19.8 | 17.6 | 13.4 | 10.8 | 7.8 |
| Peaches (CA) | 57.1 | 53.1 | 33.2 | 11.6 | 7.8 |
| Snap Beans (OR) | 9.5 | 7.0 | 0.7 | 0.3 | 0.2 |
| Tomatoes (CA) | 16.9 | 15.1 | 12.7 | 7.3 | 5.1 |

The following changes were made input parameters and scenarios used in this assessment relative to those used in the original set of estimates:

- The foliar half-life was changed from 35 to 3.71 days, based on review of available studies
- The foliar washoff coefficient was changed from a default value of 0.5 to 0.91 based on estimates made from two literature studies submitted by the registrant.

- The site for used to represent a vulnerable site for apples was changed from Oregon to Pennsylvania. (Oregon apples were still simulated for addressing endangered species concerns.)
- The soil-water partition coefficient was changed from using $K_d$'s which set by matching the texture of a measured soil to that of the texture in the soil scenario to a $K_{oc}$ of 196 L $kg^{-1}$ which better reflects current policy.
- The value used to represent microbial degradation in the pond sediment was changed from 72.2 to 216 days in keeping with current policy of parameter selection.
- The value originally used for aerobic aquatic metabolism, 12 days, unintentionally resulted in double counting of hydrolysis. A revised value of 29.6 days avoids doubling the hydrolysis rate.
- The application date on some sites was changed to better reflect the actual use practice.
- Several scenarios were added in order to address endangered species concerns on the Pacific coast at the request of Field and External Affairs Division. These were California citrus, California peaches, California tomaatoes, Oregon blackberries, and Oregon snap beans.

**Models**

These estimates were calculated using PRZM version 3.12 dated May 24, 2001 and EXAMS version 2.98.04 dated July 18, 2002. These models were run in the EFED PRZM EXAMS shell, PE3 version 1.2, dated October 15, 2002. The shell also processed the output from EXAMS to estimate the 1 in 10 year return values reported here.

It is worth noting that the Office of Pesticide Programs (OPP) is aware of an error in the current modeling system in that the peak EEC's being reported are in fact not the peaks, but 24 hour mean values on the day the peak occurs. The OPP is currently taking corrective action, but the revisions had not completed all review steps prior to initiation of this analysis. For the case of carbaryl, this likely results in an approximately five percent underestimation of the peak. However, this error is certainly covered by other substantial conservatisms which are inherent in these estimates

**Scenarios**

EEC's were calculated for 5 crops which include those which are the major use sites for carbaryl. Metadata for each scenario can be found in EFED 2002b. These sites are apples, citrus, field corn, sweet corn, and sugar beets. The scenario for apples is in Lancaster County, Pennsylvania and represents a Elioak silt loam soil, Hydrologic Group C soil. The scenario for citrus is in Collier and Hendry Counties Florida and represents a Wabasso sand soil. The scenario for field corn and sweet corn is in Darke and Rickaway Counties, Ohio and represents a Cardington silt loam soil which is Hydrologic Group C. The scenario for sugar beets is in Polk County, Minnesota. The soil there is an Adair clay loam in Hydrologic Group C.

The apple scenario in the previous modeling was set in Oregon rather than Pennsylvania. The site was switched to Pennsylvania as this site is thought to better represent a vulnerable site among all apple orchards across the United States. The Oregon site may not be protective of aquatic habitat downstream from apple orchards in the eastern United States as there is much more rain, and thus runoff during the growing season in the east.

A standard scenario for rangeland was not available. The standard scenario for wheat, which is in North Dakota in the Red River Valley was used as a surrogate. The soil there is a Bearden silty clay loam in Hydrologic Group C. There is some evidence that the rangeland being treated with carbaryl is in more arid parts of the country than North Dakota, in which case these EEC's will overestimate the exposure from this use pattern.

As noted in the introduction, six scenarios have added in order to better address the risk to endangered salmonids living on the Pacific coast. These scenarios are California citrus, California peaches, California tomatoes, Oregon blackberries, Oregon snap beans, and Oregon apples. The California citrus scenario is in the Central Valley in Fresno County. The soil is an Exeter loam, a Hydrologic Group C soil. The peach scenario was modeled with a generic fruit tree scenario in the California Central Valley. It is grown on an Exeter fine sandy loam in the same area as the citrus scenario. The tomato scenario uses a Riviera sand, also a Hydrologic Group C soil. The Oregon blackberry scenario employed the generic Oregon berry scenario and is situated in Marion County on a Group C Woodburn silt loam. The Oregon apple scenario, which also used as the base apple scenario in the original assessment is in Washington County on a Cornelius silt loam, a Group C soil. The snap bean scenario is in on Dayton soil in MRLA 2 in Oregon (a specific county was not identified. The Dayton is a Hydrologic Group D soil. A specific texture was not identified for the soil in this scenario.

**Use Patterns**

The use patterns for each crop were adapted from the carbaryl labels to represent the maximum use patterns. The input parameters used to represent these use patterns are in Table 2. These values are essentially the same as in for the previous set of EEC's except that the date of first application was changed for some crops to better represent the use pattern. For citrus, an additional EEC was estimated using an initial application date of August 31. The April 1 date appears to be plausible for Florida given the pests it is intended to control, but monitoring data in citrus watersheds in Florida indicate that the use is concentrated during August and September. The results of this run are discussed in the characterization section below. In cases where a minimum re-application interval was specified on the label this value was used to describe the maximum application pattern. In cases, when no minimum interval is specified, a interval of 3 days was used. Note that the application to peaches was made in December, as carbaryl is typically applied to dormant trees in California. Metadata for each scenario is described in EFED, 2002b.

| Table 2. Maximum label use patterns for carbaryl application on selected crops | | | | | |
|---|---|---|---|---|---|
| Crop | Single app. Rate (lb $acre^{-1}$) | Number of Applications | Application Interval | Application Method | Date of First Application |
| Apples | 2 | 5 | 3 days | aerial | June 1 |
| Citrus | 5 | 4 | 14 days | aerial | April 1 |
| Field Corn | 2 | 4 | 14 days | aerial | June 1 |
| Sweet Corn | 2 | 8 | 14 days | aerial | May 1 |
| Sugar Beets | 1.5 | 2 | 14 days | aerial | June 1 |
| Rangeland | 0.28 | 1 | -- | aerial | June 1 |
| Endangered Species Scenarios | | | | | |
| Blackberries | 2 | 5 | 7 | aerial | June 1 |
| Peaches | 7 | 2 | 3 | aerial | December 15 |
| Snap Beans | 1.5 | 4 | 7 | aerial | July 1 |
| Tomatoes | 1.98 | 4 | 7 | aerial | April 15 |

In all cases, an aerial application was used for the maximum label use pattern and the maximum reported use pattern as this is the application practice which results in the most drift from a application practice that is allowed on the label. In practice, the orchard crops would most often receive an application with by orchard air blast equipment and air blast was simulated for typical uses. Aerial application is represented by using a spray drift efficiency of 0.05 and an application efficiency of 0.95 while spray blast is represented by values of 0.03 and 0.99 for these parameters respectively. For the average use pattern, a simulated ground spray was applied to snap beans. This has a drift value of 0.01 and an application efficiency of 0.99.

Table 3 has 'average' use patterns in that the number of applications more closely reflects those that are reported by BEAD in the QUA (Hernandez, 2002). Values for 'average' were developed from estimates of the mean single application rate and total application rate for each crop. (Hernandez, 2002). Maximum reported use patterns (Table 4) were based on survey usage data available from the Doane's Agricultural Services.Maximum reported use rates were not available to complete assessments for snap beans, peaches, tomatoes and blackberries.

**Table 3.** 'Average' use patterns for carbaryl application on selected crops

| Crop | Single app. Rate (lb acre$^{-1}$) | Number of Applications | Application Interval | Application Method | Date of First Application |
|---|---|---|---|---|---|
| Apples | 1.2 | 2 | 14 days | spray blast | June 1 |
| Citrus | 3.4 | 2 | 14 days | aerial | April 30 |
| Field Corn | 1 | 2 | 14 days | aerial | June 1 |
| Sweet Corn | 3.4 | 2 | 14 days | aerial | June 1 |
| Sugar Beets | 1.5 | 1 | --- | aerial | June 1 |
| Endangered Species Scenarios | | | | | |
| Blackberries | 1.9 | 1 | -- | spray blast | June 1 |
| Peaches | 3.5 | 1 | -- | spray blast | December 15 |
| Snap Beans | 0.8 | 1 | -- | ground | July 1 |
| Tomatoes | 0.66 | 1 | -- | spray blast | April 15 |

**Table 4.** Maximum reported use patterns for carbaryl application on selected crops

| Crop | Single app. Rate (lb acre$^{-1}$) | Number of Applications | Application Interval | Application Method | Date of First Application |
|---|---|---|---|---|---|
| Apples | 1.6 | 2 | 14 days | aerial | June 1 |
| Citrus | 4.26 | 3 | 14 days | aerial | April 30 |
| Field Corn | 1.5 | 2 | 14 days | aerial | June 1 |
| Sweet Corn | 3 | 1 | --- | aerial | June 1 |
| Sugar Beets | 1.2 | 1 | --- | aerial | June 1 |

**Chemical Parameters**

The input parameters used to describe the chemical properties of carbaryl are in Table 5. In most cases these parameters were selected in accordance with guidance (Environmental Fate and Effects Division, 2002). Data quality descriptions for each parameter were derived as follows. 'Excellent' was used to describe parameters which are very well know and had little or no error associated with them ( *e.g.* molecular weight) or when there is an abundance of high quality data available. 'Very good' is used to describe parameters from high quality studies and the study is generally reproducible (*e.g.* hydrolysis) , or when there is substantial background variability (*e.g.* aerobic soil metabolism) there are multiple high quality studies used to develop the input parameter. 'Good' is used where the data is expected to be reproducible, but is more uncertain than normal, or if metabolism parameters are based on two high quality studies, or where there are multiple studies which are usable but not high quality. 'Fair' is used to describe metabolism parameters based on a single study, or where the data set is significantly flawed but still provide some usable information. Poor is used describe input parameters based on surrogate data.

In the previous modeling for aquatic exposure, soil water partitioning was by a $K_d$ values which were keyed to soil texture of measured $K_d$'s. Since texture is usually only a factor of secondary importance, this method of parameter selection would not be expected to result in great accuracy. In this assessment, a $K_{oc}$ estimated by regressing the adsorption $K_f$'s values against the organic carbon content was used. The $K_f$'s were treated as if they were $K_d$'s as according to guidance (EFED, 2002). The $K_{oc}$ value estimated using a regression model with both a slope and an intercept is significant at $p = 0.05$. However, the $K_{oc}$ model used in both PRZM and EXAMS assumes that the binding at zero organic carbon content is zero (no y-intercept). The regression to this model is significant at $p = 0.1$ but not 0.05 and results in a $K_{oc}$ estimate of 196 kg $L^{-1}$. This will result in some underestimation of the binding (and overestimation of carbaryl mobility) at low soil organic carbon contents, but greater accuracy over all scenarios.

Metabolism was estimated from three single studies for aerobic soil, aerobic aquatic and anaerobic aquatic metabolism. The aerobic soil and anaerobic aquatic metabolism half-lives were consequently multiplied by three in keeping with current policy to account for the uncertainty caused by the high background variability in these parameters. The anaerobic aquatic metabolism values was not adjusted by three in the previous assessment. Also, in the previous assessment, the aerobic aquatic metabolism input was 14.7 d, or three times the single estimate. However, this value was not adjusted to account for hydrolysis, so hydrolysis was double counted in the previous assessment. In this assessment, the expected hydrolysis rate (9.3 d) at the study pH (7.1) was subtracted from the rate constant for the measurement from the aerobic aquatic metabolism study. This value, 9.87 d, which is the half-life in the aerobic aquatic metabolism study due to metabolism alone, was multiplied by three for a value of 29.6 d.

In the original assessment, the foliar degradation half-life was set to 35 days based OPP policy for terrestrial exposure assessments in the absence of measured foliar degradation rates. Current guidance is to use a rate constant of zero for aquatic assessments in the absence of data. In the response to comments submitted by the primary registrant, Bayer CropScience, provided data (MRID 45860501) that carbaryl degrades on foliage at substantially faster rate than 35 d. The data discussed in the submission provided by the registrant was reviewed and analyzed (D288376). Based on this assessment a value of 3.71 days was used for the foliar degradation half-life. This represents an upper 90% confidence bound on the mean from 30 foliar dissipation studies.

| Table 5. Chemical input parameters for carbaryl. | | |
|---|---|---|
| Parameter | Value | Quality |
| Molecular weight | 201.22 g $mol^{-1}$ | excellent |
| Solubility | 32 mg $L^{-1}$ | good |
| Henry's Law Constant | $1.28 \times 10^{-8}$ atm-$m^{-3}$ $mol^{-1}$ | fair |
| $K_{oc}$ | 196 L $kg^{-1}$ | good |
| Aerobic soil metabolism half-life | 12 d | fair |
| Aerobic aquatic metabolism half-life | 29.6 d | fair |
| Anaerobic aquatic metabolism half-life | 216.6 d | fair |
| Hydrolysis half-life | pH 5 - assumed stable<br>pH 7 - 12 d<br>pH 9 - 0.133 d | good |
| Aqueous photolysis | 21 d | good |
| Foliar Degradation Rate | 3.71 d | excellent |
| Foliar Washoff Coefficient | 0.91 | fair |

As part of the data submitted for consideration in estimating the foliar degradation rate, the registrant also submitted data which supported a revised estimate of the foliar washoff coefficient. In the absence of data, current EFED policy recommends a washoff coefficient of 0.5, which represents the fraction of chemical that washes off with each 1 cm of rainfall. An analysis of two relevant studies indicates that washoff coefficient of 0.91 is more appropriate. However, the estimates for both studies were based on two point estimates, so no error term or determination of variability in the data could be made. A more complete description of how the studies were assessed is in the report titled *Review of "Estimation of Foliar Dissipation Half-life of Carbaryl"* (DP Barcode D288376).

**Results**

EEC's were calculated as described above for the maximum label use pattern. These adjusted EEC's were reported in Table 1. The use site with the highest EEC's is citrus. These EEC's are Tier II estimates. A Tier II EEC uses a single site which represents a high exposure scenario for the use of the pesticide on a particular crop or non-crop use site. The weather and agricultural practice are simulated at the site over multiple (in this case, 30) years so that the probability of an EEC occurring at that site can be estimated. Sites are selected to represent a site which is more vulnerable than 90% of the sites which are used for growing the crop on a nationwide basis. Sites are currently selected to meet this standard by best professional judgement. The single point estimates represent the peak or mean values that would be expected to recur every 10 years. They specific value representing the 1 in 10 years in linearly interpolated from between the third and fourth highest annual values. EEC's for typical use patterns (Table 6) and maximum reported use patterns (Table 7) are included below.

**Table 6.** EEC's for the 'average' use patterns for carbaryl on selected agricultural crops. Endangered species scenarios are for use in evaluating the risks to endangered aquatic species on the Pacific Coast.

| Crop | Peak | 4 Day Mean | 21 Day Mean | 60 Day Mean | 90 Day Mean |
|---|---|---|---|---|---|
| | ------------------------------ $\mu g\ L^{-1}$ carbaryl ------------------------------ | | | | |
| Apples (PA) | 11.8 | 9.9 | 4.6 | 2.0 | 1.4 |
| Citrus (FL) | 99.9 | 89.3 | 51.365 | 22.7 | 15.6 |
| Sweet Corn | 45.8 | 40.6 | 24.9 | 12.7 | 8.8 |
| Field Corn | 13.5 | 11.9 | 7.3 | 3.7 | 2.6 |
| Sugar beets | 6.5 | 5.8 | 3.4 | 2.1 | 1.4 |
| Endangered Species Scenarios | | | | | |
| Apples (OR) | 2.9 | 2.6 | 1.6 | 1.0 | 0.7 |
| Blackberries (OR) | 8.3 | 7.3 | 6.2 | 3.9 | 2.7 |
| Citrus (CA) | 7.3 | 6.6 | 4.3 | 2.4 | 1.6 |
| Peaches (CA) | 14.2 | 12.8 | 7.2 | 2.8 | 1.8 |
| Snap Beans (OR) | 1.2 | ~~2.0~~ 1.1 | ~~3.9~~ 0.7 | ~~2.7~~ 0.3 | ~~0.7~~ 0.2 |
| Tomatoes (CA) | 1.7 | 1.5 | 1.0 | 0.5 | 0.3 |

The standard pond scenario used here serves not only to protect ponds and small lakes but also is intended as a surrogate for a variety of small water bodies at the top of watersheds. These include prairie potholes, vernal pools, playa lakes, bogs, swamps, and other wetlands, and first order streams. Shallower static water bodies will tend to have higher concentrations as will first order streams, although the duration of these peaks in streams tends to be of much shorter duration. Because these water bodies are at the top of the watershed, the assumption of 100% cropping for the watershed, essentially one farm field, is reasonable. Water bodies further downstream will have lower concentrations due to dilution with waters coming from land which was not treated. Some watersheds may have greater treated surface area to pond volume ratio which will increase the loading of pesticide to the pond, the this effect is limited because larger watersheds are decreasingly likely to be cropped to a single crop all treated with a certain pesticide, and the associated increase in the volume of runoff water makes it more likely that there will be pesticide transported out of the pond when the pond overflows. (Pond overflow is currently not simulated in these assessments.)

**Table 7.** EEC's for the maximum reported use patterns for carbaryl on selected agricultural crops. Endangered species scenarios are for use in evaluating the risks to endangered aquatic species *on the Pacific Coast.*

| Crop | Peak | 4 Day Mean | 21 Day Mean | 60 Day Mean | 90 Day Mean |
|---|---|---|---|---|---|
| | ---------- $\mu g\ L^{-1}$ carbaryl ---------- | | | | |
| Apples (PA) | 15.8 | 13.2 | 6.2 | 1.7 | 1.8 |
| Citrus (FL) | 130.6 | 115.7 | 68.5 | 22.7 | 15.6 |
| Sweet Corn | 23.5 | 20.9 | 11.6 | 6.8 | 4.8 |
| Field Corn | 20.2 | 17.9 | 11.0 | 6.6 | 3.9 |
| Sugar beets | 5.2 | 4.6 | 2.7 | 1.7 | 1.1 |
| Endangered Species Scenarios | | | | | |
| Apples (OR) | 6.1 | 5.4 | 3.4 | 2.0 | 1.3 |
| Citrus (CA) | 16.8 | 15.0 | 11.0 | 7.4 | 5.1 |

Three additional simulations were done for Florida citrus in order to better characterize the exposure in this scenario. In the first simulation, the application date for the first application was changed from April 30 to August 31, otherwise using the maximum application practice. While there are pests which could be of concern on citrus as early as April, monitoring data from the area indicates that most of the usage actually occurs in the late summer. The 1 in ten year peak EEC for April application and maximum label practice is 130.6 while for September the value is 105.6 $\mu g\ L^{-1}$. Another run was done where best estimates for all the metabolism values were used as inputs, 4 day half-life for aerobic soil metabolism, a 9.6 day half-life for aerobic aquatic metabolism, 72.2 days for anaerobic aquatic metabolism, and 3.2 days for foliar degradation. This was combined with 'typical' application practice in September to give a 'best' estimate of the EEC for this site. The 1 in 10 year peak in this case was 61.9 $\mu g\ L^{-1}$. This value represents the value most likely to occur in vulnerable sites due the current use of the pesticide.

There are several factors which limit the accuracy and precision of this analysis including the selection of the high exposure scenarios, the quality of the input data, the ability of the models to represent the real world, and the number of years that were modeled.

A scenarios that is selected for use in Tier 2 EEC calculations is one that likely to produce large concentrations in the aquatic environment. It should represent a site that really exists and would be likely to have the pesticide in question applied to it. It should be extreme enough to provide conservative estimates of the EEC, but not so extreme that the model cannot properly simulate the fate and transport processes at the site. Currently, sites are chosen by best professional judgement to represent sites which generally produce EEC's larger than 90% of all sites used for that crop. The EEC's in this analysis are accurate only to the extent that the site represents this hypothetical high exposure site.

The quality of the analysis is directly related to the quality of the input parameters. In general, the fate data for carbaryl is good. The paucity of soil and aquatic metabolism data is the main limitation of this data set. Because metabolism values are set to the upper 90% confidence limit of the mean, the EEC's will be conservative to the extent we are uncertain of the true central tendency of the metabolism data. Additional metabolism data would greatly increase confidence, and likely reduce our EEC estimates.

The models themselves represent a limitation on the analysis quality. While the models are some of the best environmental fate estimation tools available, they have significant limitations in their ability to represent some processes. Spray drift is estimated as a straight 5% of the application rate reaching the pond for each application. In actuality, this value should vary with each application from zero to perhaps as high as 15%. A second major limitation of the models is the lack of validation at the field level for pesticide runoff. While several of the algorithms (volume of runoff water, eroded sediment mass) are well validated and well understood, there is less confidence that PRZM 3.12 well represents the amount of pesticide transported in runoff events. Some validation efforts undertaken by the pesticide industry and under review by the Agency indicate that PRZM gives reasonable estimates of pesticide extraction into runoff, but validation of the runoff portion of PRZM is not extensive. Other limitations of the models used are the inability to handle within site variation (spatial variability), no crop growth algorithms, and an overly simple soil water transport algorithm (the "tipping bucket" method).

A final limitation is that only thirty years of weather data was available for the analysis at each site. Consequently there is approximately 1 chance in 20 that the true 10% exceedence EEC's are larger than the maximum EEC in the calculated in the analysis. If the number of years of weather data could be increased, it would increase the confidence that the estimated value for the 1 in ten year exceedance EEC was close to the true value.

The EEC's presented could be improved by additional information on metabolic degradation rate as all metabolism values were based on a single study. Estimates could also be improved by more refined consideration of spray drift, this is especially so for the west coast scenarios. Better information of timing of applications and application intervals would also help refine these estimates as indicated by the additional runs done for Florida citrus.

**Literature Citations**

D288376. Jones. R. David. 2003. *Review of "Estimation of the Foliar Dissipation Half-life of Carbaryl" and Re-analysis of the Foliar Degradation Rate*. EPA Internal Memorandum to Tony Britten.

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